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MINIMIZING WOOD SHRINKAGE AND SWELLING

Treating With Synthetic Resin-Forming Materials

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Treating with Synthetic Resin-Forming Materials

By

ALFRED J. STAMM and R. M. SEBORG

A method of forming synthetic resins within the fine capillary structure of wood as a means of minimizing swelling and shrinking is described. Antishrink efficiencies as high as 70 percent have been obtained when the wood took up 30 to 50 percent of its weight of resin. Efficiencies as high as 50 percent have been obtained with as little as 15 percent increase in the weight of the wood. This efficiency is not due to a decrease in the rate of absorption of moisture, as is the case for the waxes previously described, but to an equilibrium change. Prepolymerization of the resin-forming mix before treatment decreases the antishrink efficiency. No loss in the efficiency results upon cutting the wood. The hardness and the strength across the grain of the wood are appreciably increased by the treatment. The treated wood can be satisfactorily glued, and glued specimens can be treated without affecting the glue joints.

Shrinking and swelling and the accompanying warping, checking, and honeycombing constitute the most detrimental property of wood. Considerable effort, therefore, has been recently extended to minimize the dimension changes. Studies of the effect of moisture-excluding surface coatings (2, 4) of impregnation with hygroscopic salts to retain the green condition (8) and replacement of the water within the swelling structure with waxes and natural resins using a solvent completely miscible with water and with the treating material as an intermediate replacing agent (10) have been reported from the Forest Products Laboratory. This paper gives the results of forming synthetic resins in the cell structure upon the subsequent swelling and shrinking.

Surface coatings constitute the simplest form of antishrink protection. For relatively short humidity-change cycles in which the time of exposure to a high or low relative humidity does not exceed 2 or

3 weeks, they may give surprisingly high efficiencies. Coatings of aluminum leaf between coats of other materials such as paints and varnishes have given antishrink efficiencies as high as 95 percent (4). Such a treatment, however, does not affect the hygroscopicity of the wood itself although it does greatly retard the rate of diffusion of water vapor into the wood. The antishrink efficiency consequently decreases appreciably as the time of exposure to any one condition is increased or mechanical wear takes place. The same condition has proved to be true for specimens treated throughout the coarse capillary structure by direct impregnation methods and also in the case of the replacement of water in the internal structure of the fibers with waxes, using an intermediate solvent completely miscible with both water and the waxes as a carrier for the solute (10). Although a much larger surface is filmed in these cases, water can work its way between the film and the fibers, and in general does so more readily than in the case of the one more perfectly formed external film. An extension of the previously reported replacement measurements (10) to smaller specimens which come to equilibrium more quickly, using a longer time of exposure to each relative humidity of 16 weeks, gave an antishrink efficiency of only 15 percent for stearin, whereas the efficiency of the nonpolar materials, such as paraffin, had become practically negligible. The inert material deposited in the cell wall prevents shrinkage from occurring to the original oven-dry condition, but it does allow considerable swelling to occur beyond the original green dimensions.

From these measurements the bonding of the treating material to the wood seems to be of greater importance than the actual moisture resistance of the material itself. It was thus reasonable to suppose that formation of a synthetic resin within the fine wood structure from unpolymerized polar molecules that can bond with the free hydroxyl groups of cellulose which account for its hygroscopicity (7, 9), would give far more permanent efficiencies. The following data show this to be the case.

Several investigators have studied the impregnation of wood with synthetic resins in order to change its appearance, density, mechanical properties, decay resistance, and resistance to chemicals (1, 3, 6). The possibility of reducing the swelling and shrinking has, in general, been overlooked, as the methods of treatment have been such as to affect this property but slightly.

Treatments with Resin-Forming Materials

The results of a preliminary survey made on white pine blocks 3-1/2 inches (8.9 cm.) in the direction tangent to the annual rings of the wood (the direction of maximum swelling, 7) and 7/8 inch (2.2 cm.) in the two other directions are given in Table 1 for various treating solutions:

Table 1.--Antishrink efficiencies of white pine treated with synthetic resin-forming solutions and cured at 105° C.¹

Treating solution	No. of samples		No. of treatments		Anti-shrink efficiency ²	Resin content of wood
					Percent	Weight percent
1. 250 g. phenol + 500 cc. of 40% formaldehyde + 50 cc. concd. ammonia	1	1	1	1	45.4	115
	1	2	1	1	73.9	150
	2	3	1	1	81.2	175
	1	4	1	1	90.9	178
	1	5	1	1	99.8	179
2. 33 g. phenol + 33 cc. formaldehyde + 2 g. hexa ³ + 200 cc. methanol	2	1	1	1	37.0	77.2
3. Same as 2 except solvent ethylene glycol monoethyl ether	2	1	1	1	32.0	36.2
4. Soaked in satd. hexa soln., dried, and treated with 33 g. phenol + 33 cc. formaldehyde + 200 cc. methanol	1	1	1	1	36.1	86.0
5. Same as 4 except treated with 100 g. phenol + 50 cc. formaldehyde + 150 cc. linseed oil	2	1	1	1	50.0	121
6. Same as 4 except treated with 400 g. phenol + 300 cc. linseed oil + 100 g. rosin	2	1	1	1	59.4	136
7. 50 g. phenol + 100 cc. formaldehyde + 10 cc. ammonia + 50 cc. furfural	2	2	1	1	58.0	144
8. Same as 4 except treated with 100 g. phenol + 100 cc. furfural	1	1	1	1	44.5	70.5
9. Same as 8 except 43 cc. furfural	1	1	1	1	47.5	126
10. 50 cc. furfural + 10 cc. aniline + 50 cc. linseed oil	2	1	1	1	54.4	92
11. Soaked in 2% aniline hydrochloride solution in ethylene glycol monoethyl ether, dried, and treated with 50 cc. furfural + 150 cc. linseed oil	1	1	1	1	58.6	81
12. Same as 11 except 50 cc. linseed oil	1	1	1	1	55.9	96
13. 25 g. thiourea + 50 cc. formaldehyde + 50 cc. acetaldehyde	1	1	1	1	57.6	97
14. Soaked in satd. thiourea solution at 70° C. followed by soaking in formaldehyde at room temp.	1	1	1	1	53.3	112
15. 40 g. urea + 10 g. hexa + 160 cc. water; heated over acetaldehyde in bomb at 100° C.	2	1	1	1	71.0 ⁴	65

¹These measurements were made by L. A. Hansen.

²In terms of the retardation in the dimension changes per unit dimension change of the control for the average of three 4-week relative humidity cycles between 30 and 90 percent.

³Hexamethylene tetramine.

⁴This high efficiency is due to the fact that part of the hygroscopic urea remains unpolymerized and acts as the hygroscopic salts in keeping the wood swollen (8). The moisture content at 30% relative humidity was 17½ and at 90% relative humidity, 90.5%.

Oven-dry blocks were immersed in the treating solutions at room temperature. A vacuum was applied to remove the air from the blocks and released to permit penetration until air bubbles no longer appeared. The blocks were kept in the resin-forming solution for at least a day to permit diffusion into the fine structure, and were then air-dried, followed by drying at 70° C. and curing at 105° C. for at least a day. The blocks were then placed in a 30 percent relative humidity room for 2 weeks, followed by 2 weeks in a 90 percent relative humidity room.

The results are expressed in terms of the efficiency in retarding of the dimension changes referred to the dimension changes of the controls over three complete cycles. The data indicate that a number of different resin-forming materials can be used. Some of the treatments involve an extra intermediate drying which would not be practical. Others involve the use of furfural, which colors the wood black. Urea resins, under the conditions tried, proved unsatisfactory. It was impossible to resinify the material completely, and an excess of urea remaining in the blocks caused them to take up excessive water as in the case of wood treated with hygroscopic salts (8), thus giving wet sticky blocks at higher relative humidities. The phenol resins seemed the most promising. Because of the volatility of phenol any excess would be lost on curing so that a condition similar to that cited for urea would be impossible. Phenol is the best swelling agent for wood so far tried. It opens the fine capillary structure and thus permits freer diffusion of the solute into the fine structure. It appears to have even a greater affinity than water for wood. For these reasons and because it is relatively cheap, phenol was used in these studies.

Treatments with Phenol-Formaldehyde Solutions

In Table 2 a series of tests on redwood blocks of the same size as the blocks used in the preliminary work are given:

The blocks were put through the 30 and 90 percent relative humidity cycle prior to treating so that each block served as its own control. The treatment was made after equilibrium was obtained with 30 percent relative humidity. The blocks were placed in a treating cylinder and evacuated, the resin-forming solution was run in on the blocks, and 75 pounds per square inch (5.3 kg. per sq. cm.) pressure was applied. After keeping the blocks in the treating solution for a day, they were cured for 3 days at 70° C., followed in some cases by another day at 70° C. or a day at 105° C. as indicated in Table 2. The formaldehyde was introduced either in the form of formaldehyde (40 percent solution) or of trioxymethylene. In some cases where formaldehyde was used, the solution was heated just to the temperature at which water started to separate and then it was suddenly cooled. The separated water was removed before treating or dissolving in the solvent. Both hexamethylene tetramine and ammonia were used as catalysts, the latter in the form of the concentrated aqueous solution. No significant differences were obtained with the two different catalysts.

Table 2.--Antishrink efficiencies of redwood treated with phenol-formaldehyde resin-forming solutions

Treating solution	Solvent	Resin : concentration	Curing : temp.	Anti- : shrink : effi- : ciency ¹	Resin : content : of : wood ²
		Volume : percent	°C.	Percent	Weight : percent
1. Equal weights of phenol and formaldehyde + 3% hexa ³	Methanol	50	70	28.0	41.0
2. Same as 1		50	105	40.5	47.5
3. Same as 1 + 5% ammonia		50	70	26.0	36.0
4. Same as 3		50	105	40.0	40.9
5. Equal weights of phenol and formaldehyde + 3% hexa (heated and water separated)	None	100	70	Slight : negative : value	121.0
6. Same as 5		100	105	8.5	121.0
7. Same as 5	Methanol	50	70	35.0	73.0
8. Same as 5		50	105	53.9	79.0
9. Same as 5		35	70	33.2	54.0
10. Same as 5		35	105	46.0	50.6
11. Same as 5 + 5% ammonia		50	70	37.0	62.8
12. Same as 11		50	105	48.9	69.0
13. Same as 11		35	70	34.6	40.3
14. Same as 11		35	105	44.3	41.2
15. 3 parts phenol to 1 of trioxymethylene + 5% ammonia	Methanol	35	70	39.8	62.3
16. Same as 15		35	105	49.0	56.8
17. Same as 15		50	70	35.6	80.6
18. Same as 15		50	105	51.6	85.2
19. Same as 15 + 10% ammonia		50	70	34.0	77.0
20. Same as 19		50	105	48.5	84.0

¹In terms of the retardation in the dimension changes per unit dimension change of the control for the average of four specimens exposed for three 4-week relative humidity cycles between 30 and 90 percent.

²Relative to the weight of the wood in equilibrium with 30 percent relative humidity.

³Hexamethylene tetramine.

In all cases curing at the higher temperature gave greater efficiencies, undoubtedly because of a more complete polymerization. When the treating solutions in which formaldehyde was used were heated and the water was removed, the efficiency for a fixed concentration in alcohol was increased since the proportion of the active ingredients was greater. The efficiency on the basis of the weight increase of the wood after curing, however, did not seem to vary appreciably. The use of trioxymethylene in place of formaldehyde in the system from which the water was separated also showed little effect upon the antishrink efficiency.

When the phenol-formaldehyde-hexamethylene tetramine solution, from which the water had been removed, was used to treat the wood without a solvent, low efficiencies resulted. Because of the relatively high viscosity, diffusion into the cell wall was appreciably retarded even though an appreciable penetration of the coarse capillary structure resulted, as shown by weight increase. In this case some of the resin may have polymerized in the coarse capillary structure before diffusion into the finer structure could take place. When the resin-forming solution is dissolved in alcohol, this is less likely to occur since the alcohol acts as a partial inhibitor.

Similar measurements on a number of different species of wood are given in Table 3, using phenol-formaldehyde ammonia solutions similar to those given in Table 2 (with and without water separation) and a prepared Bakelite phenol-formaldehyde mix known as Resinoid 5995 (used in both alcohol and water solutions). The Resinoid showed, on the average, the same efficiency with both solvents. In all cases it gave appreciably better efficiencies than the phenol-formaldehyde-ammonia preparation, largely because of the greater penetration as shown by a greater increase in weight of the specimens. The antishrink efficiency for the different species which are sufficiently permeable to be treated do not vary appreciably. The weight of resin taken up varies considerably more than the corresponding antishrink efficiencies since it is dependent upon the density and structure of the wood. The treatment of the heartwood of some hardwoods, such as walnut and white oak, is extremely difficult even for these small specimens and practically impossible in the case of larger specimens. The penetration of wood with these resin-forming solutions in general parallels the ease of penetration of different species with preservatives (5). The low efficiency in the case of cypress sapwood, even though the penetration was normal, cannot be explained.

Effect of Concentration of Solution and

Theoretical Antishrink Efficiency

The effect of the concentration of the resin-forming solution upon the antishrink efficiency was investigated in order to find the optimum concentrations that should be used. Figure 1 shows the increase in antishrink efficiency with increasing concentrations of Resinoid 5995 dissolved in

Table 3.--Antishrink efficiencies of various species treated with phenol-formaldehyde resin-forming solutions and cured at 105° C.

Species	Part of wood	Antishrink efficiency, ¹		Synthetic resin content of wood, ²	
		Phenol-formaldehyde-ammonia	Resinoid 5995	Phenol-formaldehyde-ammonia	Resinoid 5995
		Water	50% in	Water	50% in
		60% in separated;	50% in	60% in separated;	50% in
		methanol: 50% in	methanol: water	methanol: 50% in	methanol: water
		methanol	methanol	methanol	methanol
Softwoods					
Cypress.....	Heart	34.7	57.5	22.4	51.0
Cypress.....	Sap	16.0	24.5	39.0	73.9
Douglas fir.....	Heart	37.7	58.8	52.8	70.7
Redwood.....	Heart	41.5	65.0	50.6	95.7
Sitka spruce.....	Heart	41.6	70.4	45.9	73.8
Southern yellow pine.....	Heart	22.6	61.8	32.9	66.2
White pine.....	Heart	41.0	56.6	56.4	80.7
Hardwoods					
Ash.....	Sap	34.8	61.3	23.8	42.1
Basswood.....	Heart	47.4	64.0	54.4	104.0
Chestnut.....	Heart	30.7	62.5	48.1	79.2
Maple (sugar).....	Sap	20.7	60.2	28.4	42.7
Walnut.....	Heart	22.0	33.0	17.0	20.6
White oak.....	Heart	25.0	54.0	24.8	39.7
Average.....		32.0	56.1	38.0	57.7

¹In terms of the retardation in the dimension changes per unit dimension change of the control for the average of at least three 4-week relative humidity cycles between 30 and 90 percent.

²Relative to the weight of the wood in equilibrium with 30 percent relative humidity.

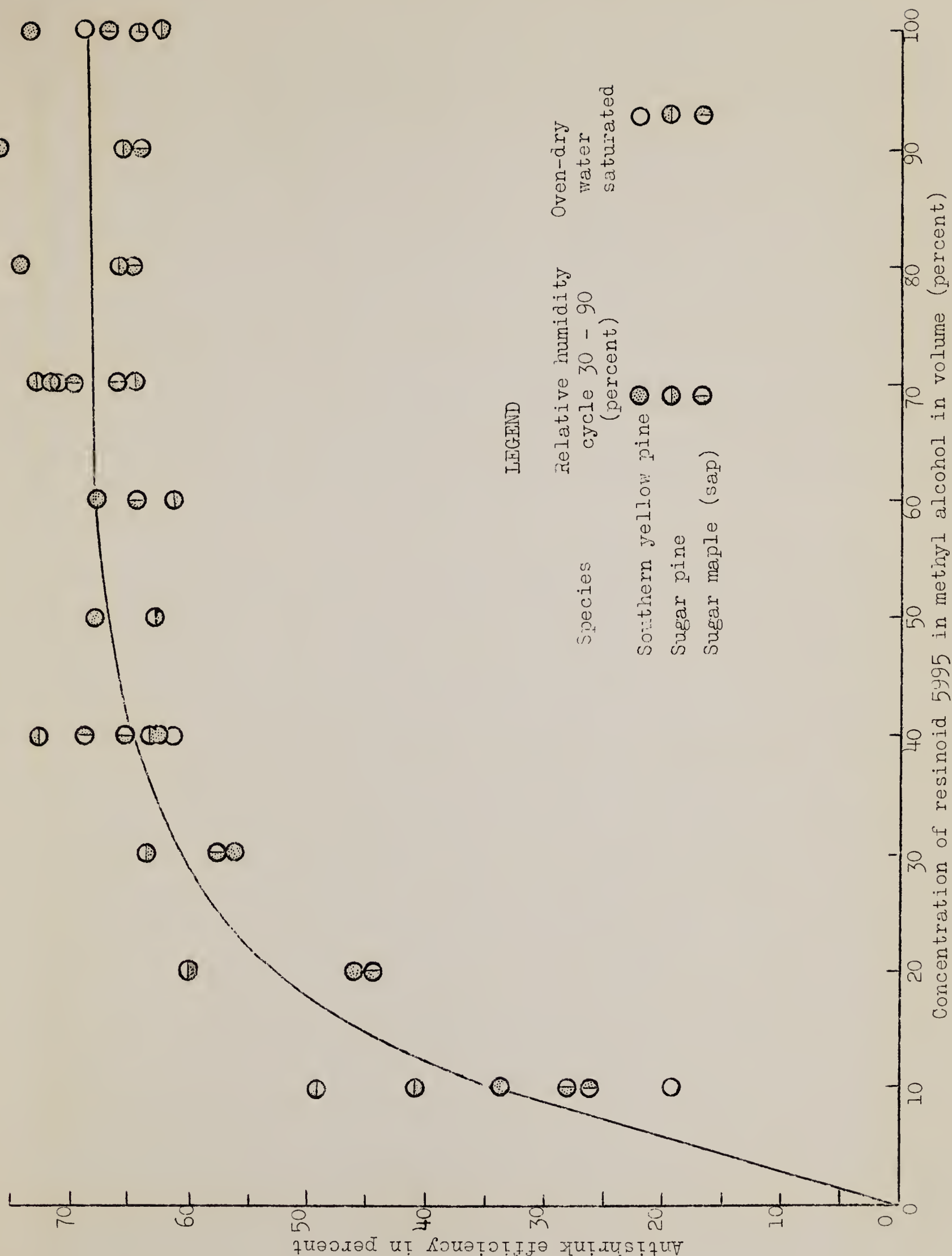


Figure 1.--Effect of concentration of resin-forming solution upon the antishrink efficiency obtained with three different species of wood.

methanol for three different species of wood. Efficiencies were calculated both from the dimension changes between 30 and 90 percent relative humidity and from the dimension changes between the oven-dry and water-soaked conditions. The antishrink efficiency increased rapidly at first with increasing concentration and finally reached a maximum value of about 70 percent. One curve satisfactorily represents the results for the three species. According to this curve it would not pay to use concentrations in excess of 20 to 30 percent. Evidently what happens is that the resin-forming material in the coarse capillary structure increases in concentration on drying of the wood and diffuses into the fine capillary structure in the same way as was found to be the case for salts (8). This diffusion will, of course, be more complete the slower the drying. Differences in the ease and distance of diffusion in the different species would account for the greater differences in the efficiencies obtained with the different species at the lower concentrations. Figure 2 shows similar results obtained with thin sections of white pine $3/32$ inch (2.4 mm.) in the fiber direction and $1-3/4$ inches (4.4 cm.) in the other two directions. These sections were conditioned in desiccators through which air, humidified by bubbling through saturated salt solutions, was passed (8).

The maximum antishrink efficiency obtained, about 70 percent, was only slightly less than the 75 percent volume contraction of the Resinoid upon polymerization (solids in Resinoid, 84 percent; density of Resinoid, 1.136; density of resin, 1.272). If the capillary structure of the cell wall is completely filled with Resinoid, the shrinkage to the cured condition should be only 25 percent of that which would have occurred in the absence of the solute. The upper curve in Figure 2 gives the actual retardation in shrinkage from the Resinoid-saturated condition to the cured condition, on the basis that the alcohol-saturated controls were corrected for the increase in the dimensions that would have resulted from the presence of the Resinoid. This curve indicates that the original Resinoid-saturated sections, in concentrations sufficient for diffusion to give 100 percent concentration of Resinoid in the fine capillary structure, shrink the theoretical amount on curing. Subsequent changes to equilibrium with 90.8, 75.8, 53.9, and 32.7 percent relative humidities followed by soaking in water and then bringing to equilibrium with 75.8 percent relative humidity gave antishrink efficiencies calculated from the cured condition as shown in Figure 2. These are all slightly less than the efficiency occurring on curing, but they are of the same order of magnitude. The subsequent swelling in water increases the dimensions slightly above the dimensions in the methanol-Resinoid solution as might be expected because water causes slightly more swelling than the alcohol. There is a slight tendency for the efficiency to be lower over lower relative humidity cycles; that is, the hygroscopicity of the treated wood relative to the controls is slightly greater at low than at high relative humidities. The antishrink efficiencies obtained between cured and 75.8 percent relative humidity after soaking were so close to the values for the same cycle before soaking that they could not be separately plotted. This reproducibility after soaking indicates that the values represent true equilibrium values. The same is indicated by long humidity-cycle

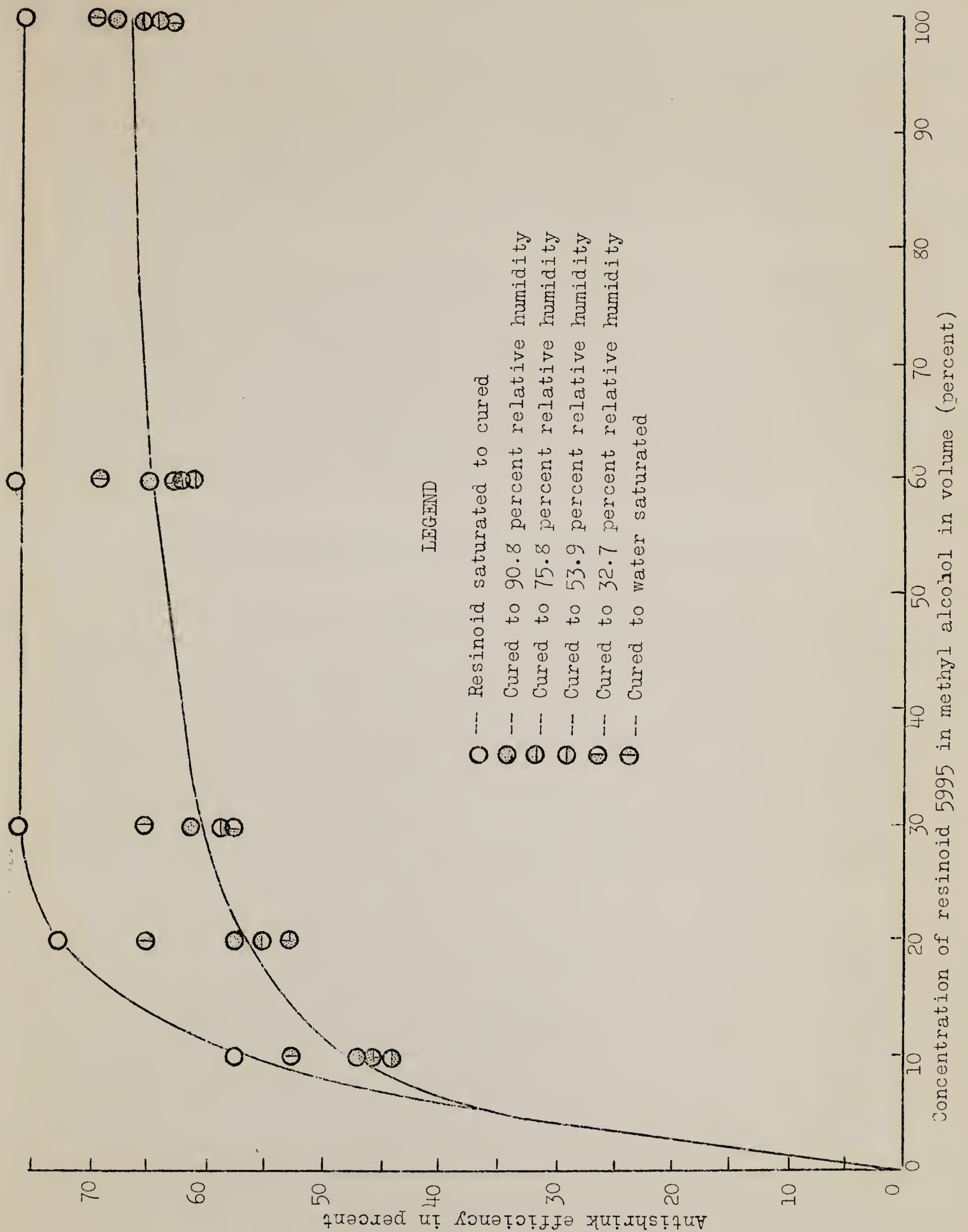


Figure 2.--Effect of the concentration of resin-forming solution and of the relative humidity cycle upon the antishrink efficiency of white pine.

measurements. When the time of exposure at high and low relative humidities was increased to 5 months, no change in the average antishrink efficiency for a series of specimens resulted. Cutting the 3-1/2 x 7/8 x 7/8 inch treated blocks across the fibers into three equal pieces did not change the antishrink efficiency obtained during subsequent relative humidity change cycles. This behavior is also a good indication that the filming of the internal cell-wall structure was complete and that the bond to the wood was exceptionally good.

As the maximum antishrink efficiency appears to be limited only by the volume contraction of the resin, it should be possible to increase the efficiency by repeated treating and curing. The same fraction of the volume within the cell wall which shrinks because of the contraction of the resin in the process of its formation should be filled after each repeated treatment. This is shown to be the case in Figure 3 in which the points represent the antishrink efficiencies after different numbers of treatments (Table 1), and the curve represents the theoretical efficiencies, assuming the efficiency of each treatment to be the same as the first.

Effect of Prepolymerization on Antishrink Efficiency

Table 4 shows the antishrink efficiency of several different commercial resins. The first two are soluble in methanol; the others are decreasingly soluble in polar solvents in the order given. The Bakelite Resinoid is a limpid liquid, the Catalin a viscous liquid, the Rezyl a plastic solid, and the last two resins are brittle solids. These properties indicate that the resins must be listed in the order of increasing degree of polymerization or decreasing polarity. Table 4 shows that a decrease in antishrink efficiency is obtained with resins of increasing degree of prepolymerization or decreasing polarity. Since these resins, with the possible exception of the first, were used in these tests for a purpose quite different from that for which they were intended, the data should not be considered as a reflection upon any of them.

Figure 4 gives the effect of prepolymerization of the Bakelite Resinoid 5995. The upper group of curves gives the antishrink efficiency after different degrees of prepolymerization in an oven at 107° C., and the lower group gives the corresponding swelling beyond the swelling in the solvent, both plotted against the concentration of the Resinoid in methanol. The sample heated for an hour and three-quarters was removed from the oven and cooled without separation of the resin. The viscosity of a 50 percent solution in methanol relative to that of the unheated sample was 1.08. The sample heated for 2 hours separated on cooling. A 50 percent solution of the total sample gave a relative viscosity of 1.35. The sample heated for 2 hours and a quarter separated in the oven. This sample was difficult to dissolve in methanol. The relative viscosity of its 50 percent solution was too high to measure with the Ostwald viscometer used. Both the antishrink

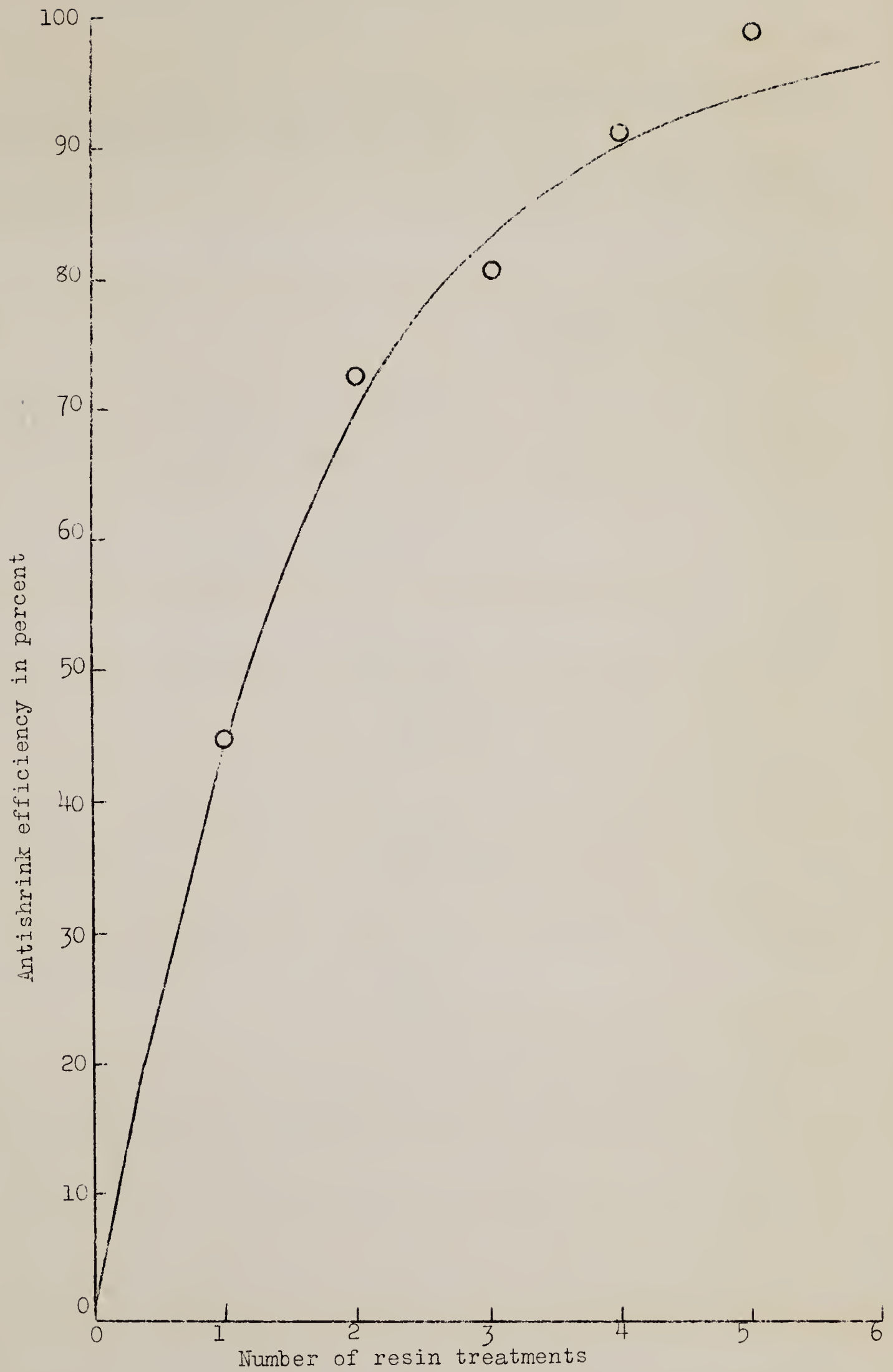


Figure 3.--Effect of number of treatments upon the antishrink efficiency of white pine.

Table 4.--Antishrink efficiency of wood treated with various commercial resin-forming solutions and cured at 105° C.

Treating material	Wood species	Solvent	Resin : concen- : tration	Anti- : shrink : effi- : ciency ¹	Synthetic : resin con- : tent of : wood ²
			<u>Volume</u> : percent	<u>Percent</u>	<u>Percent</u>
Resinoid 5995 (phenol- formaldehyde, Bakelite Corp.)	: Redwood : Southern : yellow pine : Maple	: Methanol	: 50 : : 50 : 50	: 65.0 : : 61.8 : 60.2	: 95.7 : : 66.2 : 42.7
Catalin (phenol- formaldehyde, American Catalin Corp.)	: Southern : yellow pine : Maple	: Methanol	: 50 : : 50	: 52.9 : : 57.0	: 64.0 : : 55.6
Rezyl 14A (alkyd, American Cyanamid and Chemical Corp.)	: Redwood : Redwood : : : :	: Acetone : Ethylene : glycol : monoethyl : ether	: 50 : 50 : : : :	: 20.0 : 10.0 : : : :	: 96.0 : 64.0 : : : :
Beckacite 1112 B/664 (phenol-formaldehyde Beck, Koller, and Co.)	: Redwood : : : :	: Ethylene : glycol : monoethyl : ether	: 50 : : : :	: 10.0 : : : :	: 61.0 : : : :
Victron AA (polystyrene, Naugatuck Chemical Co.)	: Redwood : : : :	: Half ace- : tone, : half : benzene	: 10 : : : :	: 0 : : : :	: 14.0 : : : :

¹In terms of the retardation in the dimension changes per unit dimension change of the control for the average of three 4-week relative humidity cycles between 30 and 90 percent.

²Relative to the weight of the wood in equilibrium with 30 percent relative humidity.

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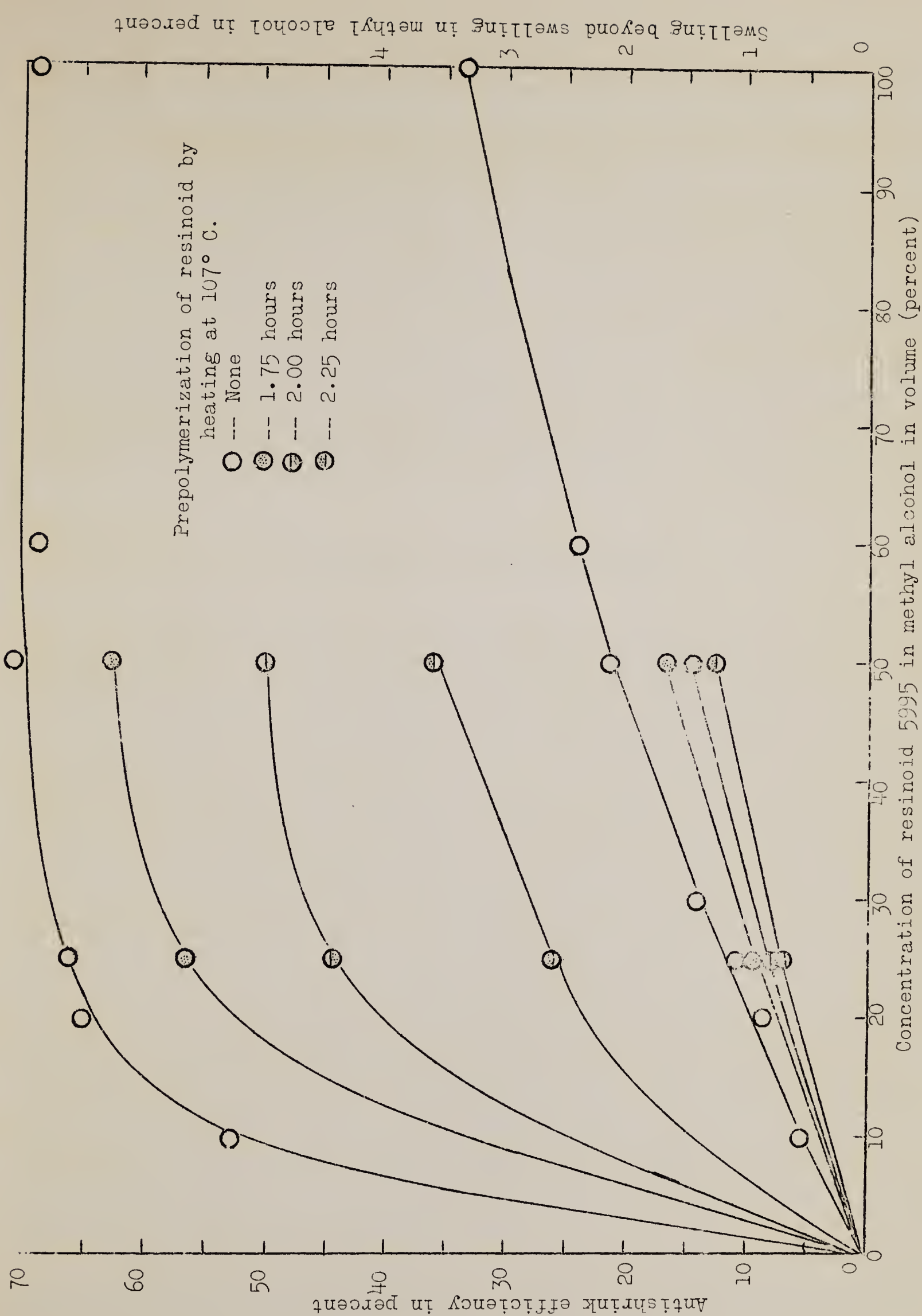


Figure 4.--Effect of degree of prepolymerization of the resin-forming solution upon the swelling of white pine beyond the solvent swollen condition and on the resulting antishrink efficiency for different concentrations of resin-forming solutions.

efficiency and the swelling beyond the solvent swollen condition decrease appreciably with prepolymerization. The swelling in the Resinoid solutions is almost a direct function of the concentration. The swelling in 100 percent unheated Resinoid is the same as the swelling of wood in a 75 percent aqueous phenol solution. This swelling beyond the solvent swollen conditions has proved to be a good index of what might be expected of a material as an anti-shrink agent. A material that does not swell wood has no affinity for the wood and hence can only affect the rate of absorption of water and not the equilibrium sorption. The unpolymerized or only slightly polymerized resin mixes are more effective in reducing the swelling and shrinking of the wood than the polymerized mixes for at least three reasons: (a) They cause greater swelling and consequently open up the structure better and bond better; (b) the smaller unpolymerized molecules diffuse into the structure much faster and more completely; (c) the small molecules can orient themselves in the structure so that polar groups satisfy a greater proportion of the points of sorption. Only a few of the polar groups of a previously formed resin molecule can fit themselves into the lattice of polar groups in the wood.

Treatment of Larger Specimens

Flat-sawn, 4 x 1 x 14 inch (10.2 x 2.5 x 35.6 cm.) boards were treated with a 50 percent solution in methanol of equal proportions of phenol and formaldehyde with 10 percent aqueous ammonia. Table 5 gives the impregnation results. The treating cylinder was evacuated for 4 hours and then the treating solution was run in on the boards. A pressure of 75 pounds per square inch was applied for 18 hours. The specimens were left submerged in the solution for 2 more days and then air dried, followed by curing at 105° C. The impregnation varied considerably among the different species because of differences in the effective capillary structure and differences in the density of the woods. The red oak was not treated uniformly, the solution chiefly entering the pore structure rather than all of the fiber cavities. The penetration of this sized specimen took place almost entirely in the longitudinal direction even though this was the long dimension of the specimens. Diffusion of the solute then took place with about equal ease in all directions from the zones that were impregnated. Although the impregnation of the coarser capillary structure of the wood prior to diffusion is not essential in getting the solute into the wood, the time of treatment would be so long when depending on diffusion alone that it would be impractical to attempt to treat wood that does not take a good impregnation treatment. The species given in Table 5 represent, in general, the more easily treated woods. The heartwood of white oak, walnut, and maple were impossible to treat except near the ends of the boards. The ends were swollen by the solution and remained in a more extended dimension condition after curing than the central portion of the boards. This resulted in severe cupping of the specimens from end to end.

Large treated specimens of wood must be carefully dried to avoid setting up stresses that result in distortion of the wood. Although the

Table 5.--Effect of species upon impregnation of flat-sawn boards with
50 percent solution of phenol-formaldehyde-ammonia in methanol

Species	Part of wood	Density: of wood (Dry)	Solution: impreg- nated	Synthetic resin content of wood after curing
			<u>Weight</u> <u>percent</u> <u>of wood</u>	<u>Weight</u> <u>percent</u>
<hr/>				
<u>Softwoods</u>				
Cypress.....	Heart	0.588	81	24
Douglas fir.....	Heart	.457	115	36
Hemlock.....	Heart	.362	203	67
Pine:				
Ponderosa.....	Sap	.455	167	48
Southern yellow.....	Heart	.575	100	25
Sugar.....	Heart	.376	193	56
White.....	Heart	.422	131	33
Redwood.....	Heart	.378	197	60
Sitka spruce.....	Heart	.427	114	36
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<u>Hardwoods</u>				
Ash.....	Heart	.605	111	37
Ash.....	Sap	.770	86	23
Basswood.....	Sap	.310	241	68
Birch.....	Heart	.677	93	24
Birch.....	Sap	.687	92	25
Chestnut.....	Heart	.490	118	32
Elm (American).....	Sap	.520	163	47
Maple (sugar).....	Sap	.716	90	21
Oak (red).....	Heart	.574	78	18
Poplar (yellow).....	Heart	.612	117	43
Poplar (yellow).....	Sap	.577	121	35
Sycamore.....	Heart	.530	106	32
Sycamore.....	Sap	.558	132	36

shrinkage from the treated to the cured condition is relatively small, steep alcohol gradients, which account for the stresses, are set up if the alcohol is allowed to evaporate too freely. The alcohol gradient will be greatly reduced and distortion practically eliminated if, in the early stages of air-drying, the wood is kept in a confined space in which an appreciable vapor pressure of the alcohol is maintained. This can be done in a chamber in which circulation of fresh air is gradually increased from zero.

Figure 5 shows the results of an analysis of the distribution of the resin in sap maple specimens, 13 inches (33 cm.) long, treated in the same manner as the previous samples. The specimen shown in curve a was cut into 1-inch (2.5 cm.) sections just after the treating and diffusion period, and each section was weighed. There is little difference in the weight of each section. The slightly lower weight of the end sections is evidently due to a slight end drying that occurred before the sections were cut. The specimen given in curve b was dried, cured, sectioned, and then weighed. To make sure that they had been completely dried, the sections were again dried (curve c) at 105° C. A slight further decrease in weight occurred. In this case there was a slight tendency for the unpolymerized resin to be carried to the ends of the specimen during the course of drying. The weights given in curve d are for the specimens of curve a after curing. The curves indicate that the combined impregnation and diffusion gave a uniform distribution of the material throughout the specimens.

Larger specimens of the permeable species than those so far tested can undoubtedly be given this antishrink treatment. The limit will naturally depend upon the time that it will pay to hold the material in treating equipment.

Effect of Resin Treatment on Mechanical and Gluing Properties

The effect of the synthetic resin treatment upon the mechanical properties of wood will only be summarized here since they will be published in more detail later. Measurements on the sapwood of sugar maple and the heartwood of sugar pine are given in Table 6. The synthetic resin increases the hardness and the compressive strength at the proportional limit perpendicular to the grain appreciably and the compression strength parallel to the grain moderately; static bending properties and toughness are hardly affected at all. The results indicate that the properties across the grain show the greatest improvement.

Gluing tests showed that the treated wood can be satisfactorily glued with animal or casein glues. Excellent results were obtained with Bakelite glues using the hot-press, but not the cold-press, technic. Plywood glued with Tego Glufilm and casein glue was successfully treated with the synthetic resin without affecting the glue joints.

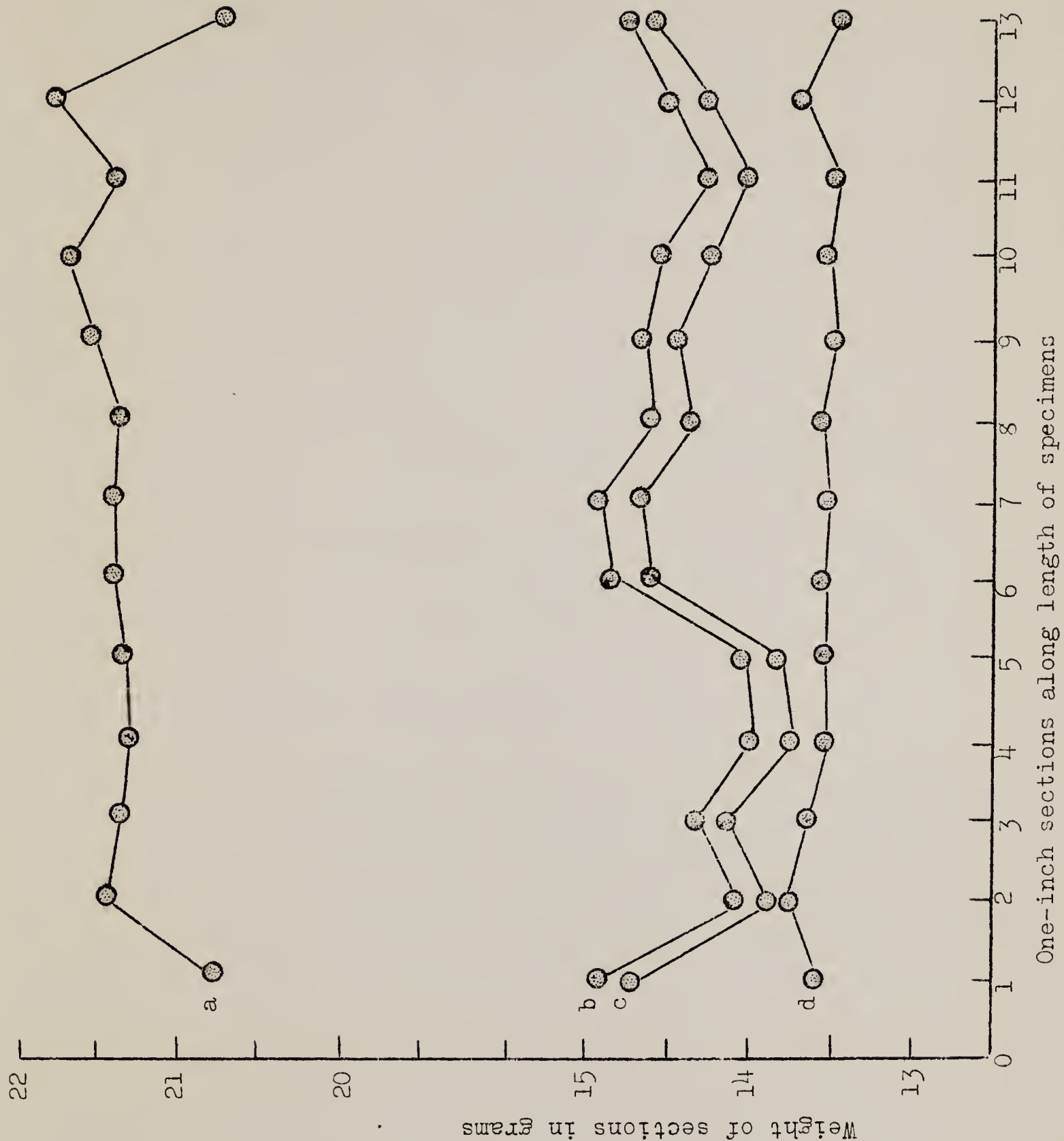


Figure 5.--Distribution of resin-forming solution and of resin along the length of a sapwood sugar maple specimen 13 inches long. (a) Weight of sections cut just after treating; (b) weight of sections cut after curing; (c) weight of (b) after further drying at 105° C.; (d) weight of sections (a) after curing.

Table 6.--Effect of phenol-formaldehyde resins on mechanical properties
of wood¹

Species	:	:	:	Com-	:	:	:	:
	:	:	:	pression:	Com-	:	:	:
	:	Resin	:	perpen-	pression	:	:	:
	:	con-	:	dicular	parallel	:	Static	:
	:	tent	:	ness	to grain,	:	Bending	:
	:	of	:	(Side):	to grain,	:	modu-	:
	:	wood	:	fiber	maximum	:	lus	:
	:	:	:	stress	crushing	:	of	:
:	:	:	propor-	strength:	:	rupture:	:	
:	:	:	tional	:	:	:	:	
:	:	:	limit	:	:	:	:	
<hr/>								
	:	<u>Weight:</u>	:	:	:	:	:	
	:	<u>percent:</u>	:	:	:	:	:	
	:	:	:	:	:	:	:	
	:	:	:	:	:	:	:	
Sugar maple	:	23.1	:	41.7	:	68.4	:	18.5
	:	:	:	:	:	:	:	2.0
(sapwood)	:	:	:	:	:	:	:	7.7
	:	:	:	:	:	:	:	-0.4
	:	:	:	:	:	:	:	:
	:	:	:	:	:	:	:	:
Sugar pine	:	47.7	:	84.7	:	52.0	:	23.5
	:	:	:	:	:	:	:	2.8
(heartwood)	:	:	:	:	:	:	:	7.4
	:	:	:	:	:	:	:	7.7
	:	:	:	:	:	:	:	:
	:	:	:	:	:	:	:	:
	:	:	:	:	:	:	:	:
	:	:	:	:	:	:	:	:
	:	:	:	:	:	:	:	:

¹In terms of the percentage increase over the values for the controls. The data represent the average values for two treated specimens, two untreated controls, and two controls that were subjected to the same heat treatment as the treated specimens cut from each of five different planks. The first values are referred to the untreated controls and the values in parentheses to the heated controls. All values are corrected to the moisture content of the untreated controls (about 6 percent moisture content).

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Literature Cited

- (1) Brajnikoff, B. J., Ind. Chemist, 6, 502 (1930).
- (2) Browne, F. L., Ind. Eng. Chem., 25, 835 (1933).
- (3) Campredon, J., Génie civil, 98, 426 (1931).
- (4) Hunt, G. M., U. S. Dept. Agr., Circ. 128 (1930).
- (5) MacLean, J. D., Ibid., Miscellaneous Pub. 224 (1935).
- (6) Shishkov, V. P., J. Applied Chem. (U. S. S. R., 8, 1043 (1935).
- (7) Stamm, A. J., Ind. Eng. Chem., 27, 401 (1935).
- (8) Stamm, A. J., J. Am. Chem. Soc., 56, 1195 (1934).
- (9) Stamm, A. J., U. S. Dept. Agr., Miscellaneous Pub. 240 (1936).
- (10) Stamm, A. J., and Hansen, L. A., Ind. Eng. Chem., 27, 1480 (1935).

